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## (54) Photocatalyst composite and process for producing the same

Zusammengesetzter Photokatalysator und Verfahren für seine Herstellung Photocatalyseur composite et procédé pour le produire

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#### Description

#### **BACKGROUND OF THE INVENTION**

#### FIELD OF THE INVENTION

The present invention relates to a photocatalyst composite comprising a substrate having photocatalyst particles adhered thereon and a process for producing the same.

#### 10 DESCRIPTION OF RELATED ART

Exposure of photocatalyst particles to an irradiation of a wavelength corresponding to not less than the band gap energy causes the photoexcitation of electrons into a conduction band with a corresponding generation of holes in a valence band. The strong reduction power of the electrons and the strong oxidation power of the holes generated by this optical excitation have been utilized in decomposition and purification of organic materials as well as in decomposition of water. The photocatalyst particles to be used in such treatments are usually deposited on a substrate of dimensions larger than the photocatalyst particles in order to prevent them from scattering into the air or exhausting out of the system and subsequently to provide for easy separation of the photocatalyst from the treatment system. The deposition of photocatalyst particles on a substrate has been accomplished by a method comprising sintering the photocatalyst particles on the substrate at a temperature of 400°C or higher to adhere the particles to the substrate, or a method comprising spraying a precursor, which can be converted to photocatalyst through thermal decomposition, onto a substrate heated at a temperature of about 400°C, thereby adhering the particles on the substrate. Alternatively, there has been proposed a method immobilizing photocatalyst particles using a certain type of fluorinated polymer. For example, Japanese patent KOKAI (Laid-open) No. Hei 4-284851 discloses a method comprising laminating a mixture of photocatalyst particles and a fluorinated polymer and compressing the laminate under a pressure. Japanese Patent KOKAI (Laidopen) No. Hei 4-334552 discloses a method comprising thermally fusing a fluorinated polymer to adhere photocatalyst particles thereto.

JP-A-5-146671 discloses a process for optically immobilizing carbon dioxide, characterized by producing an oxygen-containing hydrocarbon, by bringing carbon dioxide and water under irradiation of a ray into contact with a photocatalyst composite comprising light-transmitting porous inorganic particles having an oxide semiconductor carried thereon thermally fused with a light-transmitting fluororesin onto a light-emitting porous substrate.

Recently, an attempt has been made to use photocatalyst particles for decomposition of deleterious materials, malodorous materials and oily substances in the waste products produced daily in inhabitant circumstances as well as purification and sterilization of the waste products. Thus the photocatalyst particles have found ever broadening areas of application. In this regard, there is a need for a method capable of adhering firmly photocatalyst particles onto any substrate, which adhesion can be maintained over an extended period of time, without losing their photocatalytic function. Unfortunately, the prior art methods as described above suffer from insufficient adhesion strength as being susceptible to delamination under external pressure, and they require heating at high temperatures so that they can not apply to a substrate not resistant to heat such as plastics, interior materials such as office walls and the surfaces of various products which are difficult to heat, and the like. In addition, there are problems that the thermal treatments at high temperatures cause the photocatalyst particles to reduce their specific surface area resulting in a reduction in their photocatalytic function. Moreover, there may be required specific means such as devices for adhering under pressure, or fusing under heat.

## 45 SUMMARY OF THE INVENTION

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One object of the present invention is to provide a photocatalyst composite comprising a substrate having photocatalyst particles adhered thereon via a specific less degradative adhesive.

Another object of the present invention is to provide a process for producing the photocatalyst composite.

A further object of the present invention is to provide a coating composition using the photocatalyst composite.

### BRIEF DESCRIPTION OF THE DRAWING

Figure 1 shows variations in weight loss per unit area of the adhesives in the photocatalyst composites due to irradiation with the black light for Samples A and C from Examples and Sample E from Comparative Example.

# DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present inventors have made a research to develop a process for achieving a firm adhesion of photocatalyst particles onto any substrate over an extended period of time without damaging the photocatalytic function of the particles. As a result, the present invention has been completed on the basis of the discovery that (1) when photocatalyst particles are adhered onto a substrate with a specific adhesive, the photocatalytic function of the photocatalyst particles may decompose and deteriorate the adhesive causing the photocatalyst particles to release from the substrate, and however, the use of a specific less degradative adhesive allows adhesion of the photocatalyst particles onto any substrate without causing the release of the particles therefrom and unpredictably the photocatalyst of the present invention to exhibit sufficient photocatalytic function, (2) the photocatalyst particles may be adhere d to a substrate without lowering the photocatalytic function of the resultant photocatalyst composite when the amount of the photocatalyst particles is in the range of 5 to 98 % based on the total volume of the photocatalyst particles and the less degradative adhesive, (3) the use of adhesives of a silicon compound or cement as less degradative adhesives results in most reduced decomposition and degradation of the adhesives owing to the photocatalytic function of the photocatalyst particles so that the photocatalyst particles can be firmly adhered for a long time, (4) preferred photocatalyst particles are titanium oxide which has a high photocatalytic function, a high chemical stability and no toxicity, and that (5) a process for adhering photocatalyst particles, which is applicable to rendering relatively easily the surfaces of various products photocatalytic and which enables the photocatalytic function to be readily utilized in domestic appliances, comprises the steps of disposing photocatalyst particles and a less degradative adhesive on a substrate and then fixing the adhesive as a preferably convenient and easy process, or more particularly comprises the steps of disposing photocatalyst particles and a less degradative adhesive by coating or spraying a coating composition containing the photocatalyst particles, the adhesive and a solvent on the surfaces of a substrate such as various products and then fixing the adhesive.

That is, the present invention lies in providing a photocatalyst composite comprising any substrate having photocatalyst particles firmly adhered thereon for an extended period of time without losing the photocatalytic function of the particles.

The present invention is a photocatalyst composite comprising a substrate having photocatalyst particles adhered thereon via a less degradative adhesive, characterized in that said less degradative adhesive is a silicon compound or cement, the amount of the photocatalyst particles is in the range of 20 - 98% by volume for the silicon compound and 5 - 40% by volume for the cement based on the total amount of said photocatalyst particles and said less degradative adhesive. As used in the present invention, the term "less degradative adhesive" refers to an adhesive having an extremely reduced rate of decomposition due to the photocatalytic function possessed by the photocatalyst particles in the range of 10 % or less, preferably 5 % or less, more preferably 3 % or less, most preferably 1 % or less expressed as a weight loss of the adhesive in the photocatalyst composite as measured by the method described in the Example below. A weight loss higher than 10 % indicates undesirably vigorous decomposition or degradation of the adhesive with a great amount of the photocatalyst particles being released. The less degradative adhesives to be used in the present invention include silicon compounds such as water glass, colloidal silica, and polyorganosiloxanes, as well as cement. These adhesives may be used in combination of two or more thereof.

The cement to be used include, for example, Portland cements such as rapid-hardening cement, general-use cement, moderate heat cement, sulfate-resisting cement, white cement, oil well cement, and geothermal well cement, blended cement such as fly-ash cement, sulfated slag, silica cement, and blast furnace cement, aluminous cement and the like.

As used in the present invention, the term "photocatalyst particles" refers to those capable of exhibiting photocatalytic function upon irradiation with a radiation having a wavelength corresponding to not less than the band gap energy. The photocatalyst particles to be used include one or a combination of two or more of known metal compound semiconductors such as titanium oxide, zinc oxide, tungsten oxide, iron oxide, strontium titanate, and the like. Particularly titanium oxide which has a high photocatalytic function, a high chemical stability and no toxicity is preferred. In addition, it is preferred to include inside said photocatalyst particles and/or on the surfaces thereof at least one metal and/or a compound thereof selected from the group consisting of V, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt and Au as a second component because of the higher photocatalytic function of the resulting photocatalyst particles. The aforementioned metal compounds include, for example, metal oxides, hydroxides, oxyhydroxides, sulfates, halides, nitrates, and even metal ions. The content of the second component may vary depending upon the kind thereof. Preferred photocatalyst particles which may contain the aforementioned metals and/or metal compounds are of titanium oxide. The content of photocatalyst particles is preferably in the range of 5 to 98 % by volume based on the total amount of the photocatalyst particles and the less degradative adhesive. The content of the photocatalyst particles less than the above defined range tends undesirably to result in a reduced photocatalytic function of the resulting photocatalyst, while that higher than the above defined range tends also undesirably to cause a reduction in adhesion strength. When cements are used as less degradative adhesives, the content of the photocatalyst particles should be preferably from 5 to 40 %, most preferably from 5 to 25 %. Alternatively, when inorganic adhesives other than the cement are used as less degradative adhesives, the content of the photocatalyst particles should be preferably from 20 to 98 %, more preferably 50 to 98 % and most preferably 70 to 98 %.

The photocatalyst particles to be used in the present invention may be produced by any one of known techniques. For example, there are several methods including (1) a method comprising thermally hydrolyzing a titanium compound such as titanyl sulfate, titanium chloride, titanium alkoxides, and the like, if necessary, in the presence of seeds for nucleation, (2) a method comprising neutralizing a titanium compound such as titanyl sulfate, titanium chloride, titanium alkoxides, and the like, by adding an alkali, if necessary, in the presence of seeds for nucleation, (3) a method comprising oxidizing titanium chloride, titanium alkoxides, and the like in the vapor phase, and (4) a method comprising firing or hydrothermally treating the titanium oxides produced by any one of the methods (1) and (2). Specifically those titanium oxides obtained by the method (1) or by the hydrothermal treatment at temperatures of 100°C or higher are preferred because of their higher photocatalytic function. As used in the present invention, the term "titanium oxides" is meant to indicate those so-called hydrated titanium oxide, hydrous titanium oxide, metatitanates, orthotitanates, titanium hydroxide, besides titanium oxide, regardless of their crystal system. In order to allow at least one metal and/or compound thereof selected from the group consisting of V, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt and Au as a second component to be present inside the photocatalyst particles and/or on the surfaces thereof, one can employ a method comprising adding the metal and/or the compound to be adsorbed during the production of the photocatalyst particles, or a method comprising adding the metal and/or the compound to be adsorbed after the production of the photocatalyst particles, if necessary, under heat, or if necessary, using reduction.

The substrates to be used in the present invention include inorganic articles such as ceramics and glasses, organic articles such as plastics, elastomers, woods and paper sheets, and metallic articles made of a metal such as aluminum or an alloy such as steel. Dimensions and forms of the substrates are not critical. Even coated articles may be used.

In the present invention, it is preferred that both the photocatalyst particles and an adsorbent are adhered onto a substrate via the less degradative adhesive because there coexist an action adsorbing treatment materials. The adsorbents to be used include general adsorbents such as activated carbon, zeolites, silica gels, and the like.

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In another aspect of the present invention, a first layer consisting of an adhesive without containing any photocatalyst particles is provided on a substrate, and then a second layer consisting of a less degradative adhesive and photocatalyst particles is provided on the first layer. The provision of the first layer containing no photocatalyst particle enables a firm connection between the substrate and the second layer containing the photocatalyst particles resulting in a firmer adhesion of the photocatalyst particles onto the substrate sustainable for a longer period of time. Moreover, the first layer should preferably contain inorganic particles having no photocatalytic function as filler. Such inorganic particles to be used include those of titanium oxides, silicon oxide, aluminum oxide, magnesium oxide and the like, the surfaces of which are coated with silicon oxide, aluminum oxide, or zirconium oxide.

The photocatalyst composite according to the present invention may be produced by disposing photocatalyst particles and a less degradative adhesive on at least a part of a substrate and then fixing the adhesive to adhere the photocatalyst particles onto the substrate via the adhesive. In the present invention, specifically the photocatalyst particles and the less degradative adhesive should preferably be dispersed in a solvent to prepare a coating composition which is then coated or sprayed on a substrate to dispose the photocatalyst particles and the less degradative adhesive on at least a part of the substrate. The solvents to be used include water, and organic solvents such as toluene, alcohols, and the like. The less degradative adhesives to be contained in the coating composition include the aforementioned ones which should preferably be soluble to the solvents used. The amount of the photocatalyst particles is in the range of 5 to 98 % by volume, preferably 20 to 98 % by volume, more preferably 50 to 98 % by volume, and most preferably 70 to 98 % by volume, based on the total amount of the photocatalyst particles and the less degradative adhesive. The coating compositions may be formulated with cross linking agents, dispersants and fillers. The cross linking agents to be used include ordinary ones of isocyanate family and melamine family and the dispersants to be used include coupling agents. Particularly when the content of the photocatalyst particles in the coating composition is in the range of 40 to 98 % by volume based on the total amount of the photocatalyst particles and the less degradative adhesive, it is preferred to formulate the coating composition with a coupling agent. The amount of the coupling agents to be added should be preferably from 5 to 50 %, more preferably 7 to 30 %.

The application of the coating composition may be accomplished by coating or spraying according to any one of ordinary coating techniques including immersing, dip-coating, spin-coating, blade coating, roller coating, wire bar coating, reversal roll coating, or an ordinary spraying technique such as spray coating to dispose the photocatalyst particles and the less degradative adhesive on at least a part of the substrate. If necessary, before the application of the photocatalyst particles and the less degradative adhesive onto the substrate by coating or spraying, an organic adhesive such as acrylic resins, epoxy resins, polyester resins, melamine resins, urethane resins, alkyd resins and the like, or such a less degradative adhesive as mentioned above may be coated or sprayed onto the substrate to from a first layer and then on the first layer there is provided a second layer consisting of the photocatalyst particles and the less degradative adhesive by coating or spraying the coating composition. The organic adhesive may be of such a kind as normally used.

After coating or spraying, the composition is fixed to produce the photocatalyst composite of the present invention. The fixation may be performed by a technique of drying, irradiating with ultraviolet rays, heating, cooling, or using a cross linking agent and it is achieved at a temperature lower than 400°C, preferably from room temperature to 200°C. In this regard, a temperature higher than 400°C may undesirably cause thermal degradation of the adhesive rendering the photocatalyst particles readily releasable. The present invention prefers to employ a method for fixation with cross linking agents of isocyanate family and melamine family.

The photocatalyst composite according to the present invention can cause purification and sterilization of products containing deleterious materials, malodorous materials and oily materials as well as decomposition of such materials which come into the vicinity of the photocatalyst particles by irradiating with a ray having a wavelength corresponding to not less than the band gap energy. The radiations to be used for the exposure include light rays including ultraviolet rays, for example, the sun's rays, and lights from fluorescent lamp, black lamp, halogen lamp, xenon flash lamp, mercury lamp and the like. Particularly the light rays including near ultraviolet rays of 300 to 400 nm are preferred. The intensity and the time of irradiation with the light rays can be determined routinely depending upon the amounts of materials to be treated.

The present invention will be illustrated below with reference to some examples.

### Example 1

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To an acidic titania sol obtained by thermal hydrolysis of titanyl sulfate (CS-N, available from Ishihara Sangyo Kaisha, Ltd.), there was added sodium hydroxide to adjust the pH to 7, followed by filtration and washing. Then, to the resulting titanium oxide wet cake was added water to prepare a slurry of 100 grams/liter expressed as TiO<sub>2</sub>. Sodium hydroxide was added to this slurry to adjust the pH to 10, and then hydrothermal treatment was conducted in an autoclave at a temperature of 150°C for 3 hours. Then the slurry after the hydrothermal treatment was neutralized to pH 7 by adding nitric acid, filtered, and washed with water, followed by drying at a temperature of 110°C for 3 hours to yield titanium oxides.

Then, the mixtures of compositions indicated below were shaked in a paint shaker for one hour to effect sufficient mixing, and dispersed to produce a coating composition.

<i>30</i> .		
	Titanium oxides	9.8 grams
	Polyorganosiloxane based inorganic adhesive (a mixture of T2202A and T2202B in a ratio of 3:1, available from Japan Synthetic Rubber Co., Ltd.)	2.7 grams
35	Isopropyl alcohol	21.5 ml

The coating composition of the above formulation was coated on a glass plate of 20 cm<sup>2</sup>, and then dried at a temperature of 180°C for 10 minutes to produce a photocatalyst composite of the present invention (Sample A). This Sample A had a titanium oxide content of 90 % by volume based on the total amount of the titanium oxides and the less degradative adhesive.

## Example 2

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To an acidic titania sol obtained by thermal hydrolysis of titanyl sulfate (CS-N, available from Ishihara Sangyo Kaisha, Ltd.), there was added sodium hydroxide to adjust the pH to 7, followed by filtration and washing. Then, the resulting titanium oxide wet cake was dried at a temperature of 110°C for 3 hours to obtained titanium oxides.

Then, the mixtures of compositions indicated below were shaked in a paint shaker for 3 hours to effect sufficient mixing, and dispersed to produce a coat composition.

ſ	Titanium oxides	7.0 grams
	Polyorganosiloxane based inorganic adhesive (a mixture of T2202A and T2202B in a ratio of 3:1, available from Japan Synthetic Rubber Co., Ltd.)	4.3 grams
	Isopropyl alcohol	22.5 ml

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The coating composition of the above formulation was coated on a glass plate of 20 cm<sup>2</sup>, and then dried at a temperature of 180°C for 10 minutes to produce a photocatalyst composite of the present invention (Sample B). This Sample B had a titanium oxide content of 80 % by volume based on the total amount of the titanium oxides and the less degradative adhesive.

### Comparative Example 1

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By using the same titanium oxides as used in Example 1, the mixtures of compositions indicated below were shaked in a paint shaker for one hour to effect sufficient mixing, and dispersed to produce a coating composition.

Titanium oxides	9.8 grams
Vinyl acetate-acryl copolymer (BONCOAT 6290, available from Dainippon Ink & Chemicals, Inc.)	0.7 gram
Water	24.8 ml

The coating composition of the above formulation was coated on a glass plate of 20 cm<sup>2</sup>, and then dried at a temperature of 120°C for 10 minutes to produce a photocatalyst composite (Sample C). This Sample C had a titanium oxide content of 90 % by volume based on the total amount of the titanium oxides and the adhesive.

The photocatalyst composites obtained in Examples and Comparative Example (Samples A to C) were exposed to the black light at an ultraviolet intensity of 7 mW/cm² on the surface of each Sample for 5 hours. The adhesive in the photocatalyst composite was weighed before and after the irradiation with the black light to determine the weight loss.

As a result, no weight loss was observed for the Samples A and B of the present invention indicating no decomposition of the adhesives. However, the Sample C of the Comparative Example without using any less degradative adhesive exhibited a weight loss of 85 % indicating that most of the adhesive was decomposed by the photocatalytic function of titanium oxides. In addition, it was observed that the Sample C was yellowed and the titanium oxide particles were partly released. The variation in the weight loss of the adhesive in the photocatalyst composite owing to the irradiation with the black light for Sample A from Example 1 and the Sample E from Comparative Example is shown in FIGURE 1.

Next, each of the Samples A and B of the present invention was placed in a 3 liters glass vessel and acetaldehyde as a malodorous component was added to the vessel to a concentration of 90 ppm and then the vessel was sealed. Then, the vessel was exposed to a mercury lamp at an ultraviolet intensity of 14 mW/cm² on the surfaces of each Sample for 60 minutes. After the irradiation, the concentration of acetaldehyde in the glass vessel was measured. The results are indicated in Table 1. The Samples A and B achieved an efficient decomposition of acetaldehyde due to the photocatalytic function of titanium oxides.

Table 1

	Sample	Concentration of acetal- dehyde (ppm)
Example 1	Α	30.0
Example 2	В	0.5

## Example 3

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To an acidic titania sol obtained by thermal hydrolysis of titanyl sulfate (CS-C, available from Ishihara Sangyo Kaisha, Ltd.), there was added sodium hydroxide to adjust the pH to 7, followed by filtration, washing, drying, and then pulverizing to produce titanium oxides. 0.2 gram of the titanium oxides, 0.8 gram of white cement (available from Onoda Cement Co., Ltd.) and 0.7 gram of water were mixed and the whole was coated on a glass plate of an area of 50 cm<sup>2</sup> and dried at room temperature to produce a photocatalyst composite of the present invention (Sample D). This Sample D had a titanium oxide content of 17 % by volume based on the total amount of the titanium oxides and the less degradative adhesive.

## Example 4

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The same procedure as in Example 3, except that 0.8 gram of DENCA high alumina cement (Hi, available from DENKI KAGAKU KOGYO K.K.) was employed instead of the white cement, was repeated to produce a photocatalyst composite of the present invention (Sample E). This Sample E had a titanium oxide content of 17 % by volume based on the total amount of the titanium oxides and the less degradative adhesive.

## Comparative Example 2

1.0 gram of the same white cement as used in Example 3 and 0.7 gram of water were mixed and the whole was coated on a glass plate having a surface area of 50 cm<sup>2</sup> and dried to produce Sample F.

## Comparative Example 3

1.0 gram of the same DENCA high alumina cement as used in Example 4 and 0.7 gram of water were mixed and the whole was coated on a glass plate having a surface area of 50 cm<sup>2</sup> and dried to produce Sample G.

Each of the Samples D to G from Examples and Comparative Examples was placed in a 4 liters vessel and standard nitrogen monoxide gas was injected into the vessel. Then, the vessel was exposed to the rays from the black light at an ultraviolet intensity of 1 mW/cm² on the surfaces of each Sample and the concentration of NOx gases in the glass vessel was measured with time by means of a NOx sensor (11L, available from GASTEC Co. Ltd.). The results are indicated in Table 2. The Samples D and E from Examples 3 and 4 caused a great reduction in NOx gas concentration, while the Samples F and G from Comparative Examples 2 and 3 caused little variation in NOx gas concentration. It has been found from this fact that the photocatalyst of the present invention is effective for removing nitrogen monoxide by oxidation thereof. In the procedure as described above, the weight of the cement in each of the Samples D and E was measured to evaluate the weight loss of the cement. No weight loss was observed indicating no decomposition of the cement.

Table 2

		lable 2			
	Sample	Concentration of NOx (ppm) after			
		0 min.	10 min.	20 min.	30 min.
Example 3	D	18.8	8.9	3.1	1.2
Example 4	E	13.5	0.3	0	0
Comp. Example 2	F	15.5	13.5	13.5	13.5
Comp. Example 3	G	13.5	13.2	10.6	10.6

The photocatalyst composite of the present invention comprises a substrate having photocatalyst particles thereon via a less degradative adhesive as defined above and causes very little decomposition and degradation of the adhesive owing to the photocatalytic function. The present invention enables long-term firm adhesion of photocatalyst particles onto any substrate without damaging the photocatalytic function. The utilization of the photocatalyst composite of the present invention allows effective and prompt removal of deleterious materials, malodorous materials, oily components, bacteria, actinomyces, fungi, algae and the like. Therefore, the photocatalyst composite is very useful as deodorant and sterilizer both at home and in industry. In addition, the photocatalyst composite of the present invention can be used for an extended period of time, has a high degree of safety, finds applicability to a wide variety of deleterious materials, and is disposable without polluting the environment. Thus, it is very useful in industry.

The process for producing the photocatalyst composite according to the present invention is a useful process which can employ any materials such as plastics as substrate and produce conveniently and easily consistent quality photocatalyst composites.

The coating composition of the present invention can be coated or sprayed onto substrates of any form or desired sites thereof, and allows the ready utilizing of the photocatalytic function. Thus, particularly it is useful for domestic applications.

### Claims

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1. A photocatalyst composite comprising a substrate having photocatalyst particles adhered thereon via a less deg-

radative adhesive, characterized in that said less degradative adhesive is a silicon compound or cement, the amount of the photocatalyst particles is in the range of 20-98% by volume for the silicon compound and 5-40% by volume for the cement based on the total amount of said photocatalyst particles and said less degradative adhesive.

- 2. The photocatalyst composite according to Claim 1, wherein said photocatalyst particles and an adsorbent are adhered to the substrate via said less degradative adhesive.
- 3. The photocatalyst composite according to Claim 1, wherein on the substrate is provided a first layer comprising an adhesive without containing any photocatalyst particles and further on said first layer is provided a second layer comprising the less degradative adhesive and the photocatalyst particles.
  - 4. The photocatalyst composite according to Claim 3, wherein the adhesive of said first layer is a less degradative adhesive.
  - 5. The photocatalyst composite according to Claim 3, wherein said first layer consists of a less degradative adhesive and inorganic particles.
  - 6. The photocatalyst composite according to Claim 1, wherein said photocatalyst particles are of titanium oxide.
  - 7. The photocatalyst composite according to Claim 1, wherein said photocatalyst particles contain at least one selected from the group consisting of metals and metal compounds of V, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt and Au as a second component inside said photocatalyst particles and/or on the surfaces thereof.
- 8. A process for producing a photocatalyst composite, by disposing photocatalyst particles and an adhesive on a substrate and then solidifying the adhesive to adhere the photocatalyst particles via the adhesive, characterized in that said adhesive is a less degradative one which is a silicon compound or cement, the amount of said photocatalyst particles is in the range of 20-98% by volume for the silicon compounds and 5-40% by volume for the cements based on the total amount of said photocatalyst particles and said less degradative adhesive.
  - 9. The process for producing a photocatalyst composite according to Claim 8, wherein the disposing of said photocatalyst particles and said less degradative adhesive is accomplished by coating or spraying a coating composition consisting of a dispersion of said photocatalyst particles and said less degradative adhesive in a solvent on said substrate.
  - 10. The process for producing a photocatayst composite according to Claim 8, which comprises the steps of providing a first layer of an adhesive free from photocatalyst particles on a substrate by coating said substrate with said adhesive and fixing said adhesive onto said substrate, and then providing a second layer comprising a less degradative adhesive and the photocatalyst particles on said first layer by disposing said less degradative adhesive and said photocatalyst particles on said first layer and then fixing said adhesive and photocatalyst particles on said first layer.
  - 11. A coating composition characterized by comprising a dispersion of photocatalyst particles and a less degradative adhesive in a solvent, said adhesive being a silicon compound or cement, the amount of said photocatalyst particles being in the range of 20-98% by volume for the silicon compounds and 5-40% by volume for the cements based on the total amount of said photocatalyst particles and said less degradative adhesive.
  - 12. The coating composition according to Claim 11, comprising a dispersion of the photocatalyst particles, a less degradative adhesive and a coupling agent in a solvent.

### **Patentansprüche**

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1. Photokatalysatorkompositwerkstoff, umfassend ein Substrat mit darauf mit Hilfe eines weniger stark abbaubaren Klebstoffs zum Haften gebrachten bzw. befestigten Photokatalysatorteilchen, dadurch gekennzeichnet, daß der weniger stark abbaubare Klebstoff aus einer Siliciumverbindung oder einem Zement besteht und die Menge der Photokatalysatorteilchen im Bereich von 20-98 Vol.-% für die Siliciumverbindung bzw. 5-40 Vol.-% für den Zement, jeweils auf der Basis der Gesamtmenge der Photokatalysatorteilchen und des weniger stark abbaubaren Klebstoffs liegt.

- 2. Photokatalysatorkompositwerkstoff nach Anspruch 1, wobei mit Hilfe des weniger stark abbaubaren Klebstoffs an dem Substrat die Photokatalysatorteilchen und ein Adsorptionsmittel zum Haften gebracht bzw. befestigt sind.
- 3. Photokatalysatorkompositwerkstoff nach Anspruch 1, wobei auf dem Substrat eine erste, einen Klebstoff umfassende Schicht ohne einen Gehalt an irgendwelchen Photokatalysatorteilchen und ferner auf der ersten Schicht eine den weniger stark abbaubaren Klebstoff und die Photokatalysatorteilchen umfassende zweite Schicht vorgesehen sind.
- 4. Photokatalysatorkompositwerkstoff nach Anspruch 3, wobei der Klebstoff der ersten Schicht aus einem weniger stark abbaubaren Klebstoff besteht.
  - 5. Photokatalysatorkompositwerkstoff nach Anspruch 3, wobei die erste Schicht aus einem weniger stark abbaubaren Klebstoff und anorganischen Teilchen besteht.
- 6. Photokatalysatorkompositwerkstoff nach Anspruch 1, wobei die Photokatalysatorteilchen aus Titanoxid bestehen.
  - 7. Photokatalysatorkompositwerkstoff nach Anspruch 1, wobei die Photokatalysatorteilchen in ihrem Inneren und/oder auf ihren Oberflächen mindestens eine Komponente, ausgewählt aus der Gruppe Metalle und Metallverbindungen (von) V, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt und Au als zweite Komponente enthalten.
- 8. Verfahren zur Herstellung eines Photokatalysatorkompositwerkstoffs durch Aufbringen von Photokatalysatorteil-chen und eines Klebstoffs auf ein Substrat und anschließendes Verfestigen des Klebstoffs zur Befestigung der Photokatalysatorteilchen mit Hilfe des Klebstoffs, dadurch gekennzeichnet, daß der Klebstoff auf einem weniger stark abbaubaren Klebstoff in Form einer Siliciumverbindung oder eines Zements besteht und die Menge an den Photokatalysatorteilchen im Bereich von 20-98 Vol.-% für die Siliciumverbindungen bzw. 5-40 Vol.-% für die Zementsorten, jeweils auf der Basis der Gesamtmenge der photokatalysatorteilchen und des weniger stark abbaubaren Klebstoffs liegt.
- 9. Verfahren zur Herstellung eines photokatalysatorkompositwerkstoffs nach Anspruch 8, wobei das Aufbringen der Photokatalysatorteilchen und des weniger stark abbaubaren Klebstoffs durch Auftragen oder -sprühen einer Beschichtungsmasse, bestehend aus einer Dispersion der Photokatalysatorteilchen und des weniger stark abbaubaren Klebstoffs in einem Lösungsmittel, auf das Substrat bewerkstelligt wird.
- 10. Verfahren zur Herstellung eines Photokatalysatorkompositwerkstoffs nach Anspruch 8 durch Bereitstellen einer ersten, von Photokatalysatorteilchen freien Klebstoffschicht auf einem Substrat durch Beschichten des Substrats mit dem Klebstoff und Fixieren des Klebstoffs auf dem Substrat und anschließendes Bereitstellen einer zweiten Schicht, umfassend einen weniger stark abbaubaren Klebstoff und die Photokatalysatorteilchen auf der ersten Schicht durch Aufbringen des weniger stark abbaubaren Klebstoffs und der photokatalysatorteilchen auf die erste Schicht und anschließendes Fixieren des Klebstoffs und der photokatalysatorteilchen auf der ersten Schicht.
  - 11. Beschichtungsmasse, dadurch gekennzeichnet, daß sie eine Dispersion von Photokatalysatorteilchen und eines weniger stark abbaubaren Klebstoffs in einem Lösungsmittel umfaßt, wobei der Klebstoff aus einer Siliciumverbindung oder einem Zement besteht und die Menge an den photokatalysatorteilchen im Bereich von 20-98 Vol.-% für die Siliciumverbindungen bzw. 5-40 Vol.-% für die Zementsorten, jeweils auf der Basis der Gesamtmenge an den photokatalysatorteilchen und dem weniger stark abbaubaren Klebstoff, liegt.
  - 12. Beschichtungsmasse nach Anspruch 11, umfassend eine Dispersion der photokatalysatorteilchen, einen weniger stark abbaubaren Klebstoff und ein Kupplungsmittel in einem Lösungsmittel.

### Revendications

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- 1. Photocatalyseur composite comprenant un substrat sur lequel on a fait adhérer des particules de photocatalyseur au moyen d'un adhésif moins dégradable, caractérisé en ce que ledit adhésif moins dégradable est un composé de silicium ou un ciment, la quantité des particules de photocatalyseur est comprise entre 20 et 98% en volume pour le composé de silicium et entre 5 et 40% en volume pour le ciment par rapport à la quantité totale desdites particules de photocatalyseur et dudit adhésif moins dégradable.
- 2. Photocatalyseur composite selon la revendication 1, dans lequel on a fait adhérer lesdites particules de photoca-

talyseur et un adsorbant sur le substrat via ledit adhésif moins dégradable.

- 3. Photocatalyseur composite selon la revendication 1, où sur le substrat est disposée une première couche comprenant un adhésif et ne contenant aucune particule de photocatalyseur, et ensuite sur ladite première couche est disposée une seconde couche comprenant l'adhésif moins dégradable et les particules de photocatalyseur.
- 4. Photocatalyseur composite selon la revendication 3, dans lequel l'adhésif de ladite première couche est un adhésif moins dégradable.
- 5. Photocatalyseur composite selon la revendication 3, dans lequel ladite première couche est constituée d'un adhésif moins dégradable et de particules inorganiques.
  - 6. Photocatalyseur composite selon la revendication 1, dans lequel lesdites particules de photocatalyseur sont composées d'oxyde de titane.
  - 7. Photocatalyseur composite selon la revendication 1, dans lequel lesdites particules de photocatalyseur contiennent au moins élément choisi dans le groupe constitué des métaux et des composés métalliques de V, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt et Au en tant que second composant à l'intérieur desdites particules de photocatalyseur et/ou sur les surfaces de celles-ci.
  - 8. Procédé pour produire un photocatalyseur composite, par dépôt de particules de photocatalyseur et d'un adhésif sur un substrat puis par solidification de l'adhésif pour faire adhérer les particules de photocatalyseur via l'adhésif, caractérisé en ce que ledit adhésif est un adhésif moins dégradable qui est un composé de silicium ou un ciment, la quantité desdites particules de photocatalyseur est comprise entre 20 et 98% en volume pour les composés de silicium et entre 5 et 40% en volume pour les ciments par rapport à la quantité totale desdites particules de photocatalyseur et dudit adhésif moins dégradable.
  - 9. Procédé de production d'un photocatalyseur composite selon la revendication 8, dans lequel la mise en place desdites particules de photocatalyseur et dudit adhésif moins dégradable est accomplie par enduction ou pulvérisation d'une composition de revêtement constituée d'une dispersion desdites particules de photocatalyseur et dudit adhésif moins dégradable dans un solvant sur ledit substrat.
  - 10. Procédé de production d'un photocatalyseur composite selon la revendication 8, qui comporte les étapes consistant à disposer une première couche d'un adhésif dépourvue de particules de photocatalyseur sur un substrat en revêtant ledit substrat dudit adhésif et en fixant ledit adhésif sur ledit substrat, puis à disposer une seconde couche comprenant un adhésif moins dégradable et les particules de photocatalyseur sur ladite première couche, puis en fixant ledit adhésif et lesdites particules de photocatalyseur sur ladite première couche, puis en fixant ledit adhésif et lesdites particules de photocatalyseur sur ladite première couche.
- 11. Composition de revêtement caractérisée par le fait qu'elle contient une dispersion de particules de photocatalyseur et un adhésif moins dégradable dans un solvant, ledit adhésif étant un composé de silicium ou un ciment, la quantité desdites particules de photocatalyseur étant comprise entre 20 et 98% en volume pour les composés de silicium et entre 5 et 40% en volume pour les ciments par rapport à la quantité totale desdites particules de photocatalyseur et dudit adhésif moins dégradable.
  - 12. Composition de revêtement selon la revendication 11, comprenant une dispersion des particules de photocatalyseur, un adhésif moins dégradable et un agent de couplage dans un solvant.

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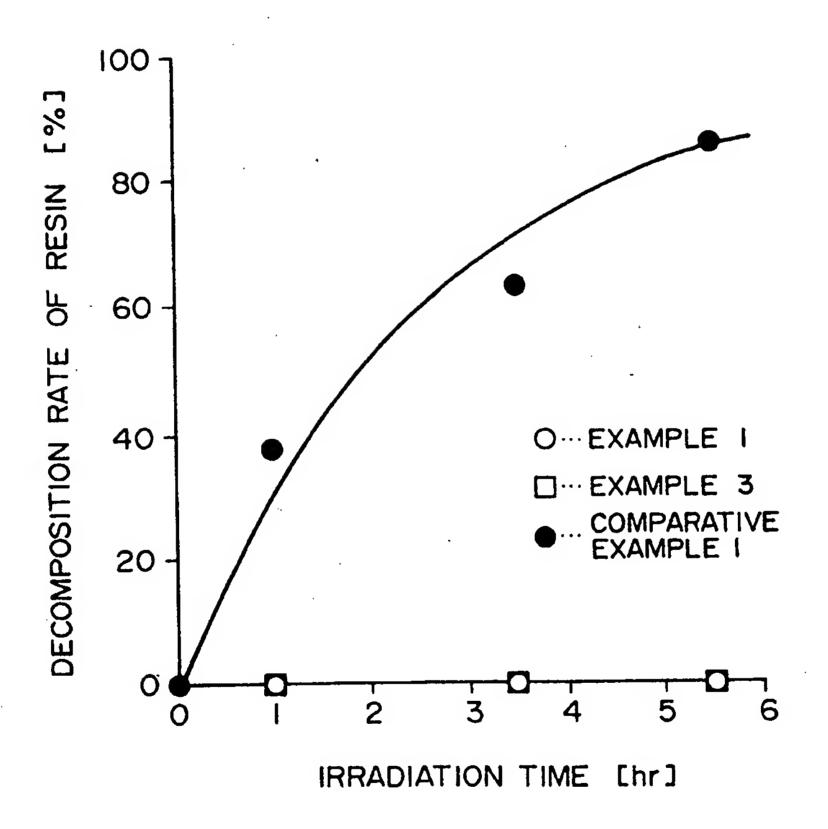
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FIG. I



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